Photo-induced 1:1:1 Reactions of 1,2,4,5-Tetracyanobenzene–Aromatic Compounds–Methanol Systems

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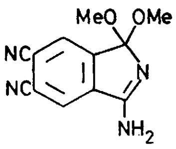
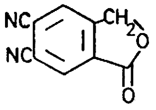
Summary Benzene, phenanthrene, or anthracene react upon irradiation with 1,2,4,5-tetracyanobenzene in methanol to give the corresponding 1 : 1 : 1 addition-elimination products.

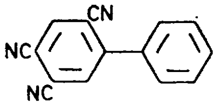
Although 1,2,4,5-tetracyanobenzene (TCNB) reacts with toluenes upon irradiation through electron-transfer followed by proton-transfer to give substitution products,[1] the TCNB–benzene system is photochemically stable under similar conditions owing to the lack of a proton source in the molecules. We now report that phenanthrene and anthracene as well as benzene react with TCNB in the presence of methanol and give the corresponding 1 : 1 : 1 addition-elimination products. While the catalytic action of methanol has been demonstrated in many cases,[2] there have been only a few reports on the formation of such 1 : 1 : 1 adducts in the photochemical reactions of electron donor–acceptor systems.[3]



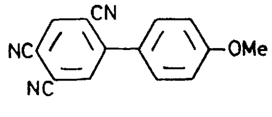
(I)



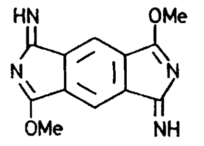
(II)



(III)

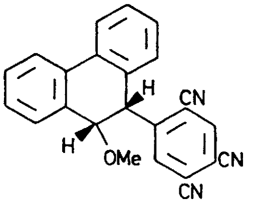


(IV)

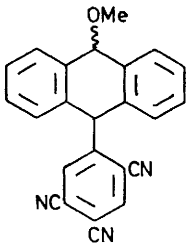


(V)

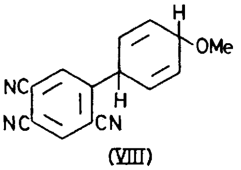
Irradiation of a solution of TCNB (0·0036 M) in benzene–methanol (1 : 1) with a Pyrex-filtered medium-pressure mercury arc for 4 h gave (I) [m.p. 125—140 °C (decomp.), 41%], (II) [m.p. 230—238 °C (decomp.), 6%], and the biphenyls (III) (m.p. 260—261 °C, 5%) and (IV) (m.p. 238—239 °C, 4%).† Their structures are based on analytical and spectroscopic data. Compound (I) was also obtained in the corresponding thermal reaction; when a similar mixture was refluxed for 20 min (I) was obtained in high yield. Structure (V)[4] had previously been assigned to (I) but the spectroscopic data of this compound, i.r. 2230 and 1675 cm^{-1}, and n.m.r. δ 8·40 (1H, s) and 8·20 (1H, s), clearly indicate the presence of C≡N and C=N groups as well as an unsymmetrically substituted aromatic unit. Treatment of this compound with HCl gave 4,5-dicyanophthalimide in good yield. We accordingly assigned structure (I) instead of (V) to the product. When the photochemical reaction was carried out below 0 °C, (I) was isolated only in small quantities. Therefore, the formation of (I) in the photochemical reaction is independent of the excited-state reaction.



(VI)



(VII)



(VIII)

To elucidate the reaction mechanism we examined other aromatic systems. Irradiation of a mixture of phenanthrene (0·0056 M) and TCNB (0·0027 M) in methanol with a low-pressure mercury arc gave an adduct (VI), m.p. 181—183 °C, in 11% yield.‡ The *cis*-arrangement of the substituents was deduced from coupling constant data: δ 5·12 (1H, d, *J* 4 Hz) and 4·65 (1H, d, *J* 4 Hz).§

Similarly irradiation of anthracene and TCNB with a low-pressure mercury arc gave an adduct (VII), m.p. 150 °C (decomp.), in 6% yield together with anthracene dimer (28%). The configuration of (VII) has not been assigned but no stereoisomers were detected in the reaction mixture.

Two mechanisms are conceivable for the formation of the adducts (VI) and (VII). Since the formation of radical cation–radical anion pairs upon irradiation is well known in the TCNB-aromatic systems,[5] and since protonation of a radical anion is very favourable,[6] it is assumed that proton-transfer from methanol to TCNB radical anion occurs initially, followed by nucleophilic attack of the methoxide ion on the aromatic radical cation, coupling of the resulting radicals, and then elimination of HCN, as shown in the

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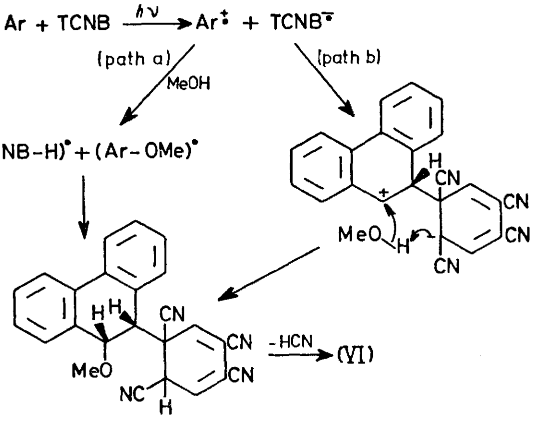
† Irradiation of a similar mixture with a low-pressure mercury lamp gave (III), (IV), and lower yields of other compounds whose structures have not been assigned; only small amounts of (II) were detected.

‡ Percentage yields are based on unrecovered TCNB.

§ When a similar mixture was irradiated with a Pyrex-filtered medium pressure mercury arc, 9-cyano- and 9-cyano-9,10-dihydrophenanthrene were obtained in 25 and 18% yields, respectively. The formation of these compounds is accounted for by the nucleophilic attack of a cyanide ion on the radical cation of phenanthrene; K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Chem. Comm.*, 1975, 553.



Scheme

Scheme (path a). Alternatively, as with the benzene—maleic anhydride system,[7] the first step is coupling of the radical anion–radical cation pair leading to a zwitterion to which methanol then adds (Scheme, path b). The stereospecific addition in the formation of (VI) seems to indicate that the latter process is preferred.

Although the TCNB–benzene or TCNB–benzene–acetonitrile system is photochemically stable, the formation of (III) in the case of the TCNB–benzene–methanol system may be accounted for by the well known catalytic action of a proton donor.[2] Since anisole did not react with TCNB under similar conditions, the adduct (IV) probably resulted from a similar 1:1:1 addition–elimination *via* an intermediate such as (VIII) which is analogous to (VI) or (VII). The formation of product (II), however, suggests that a radical route to (II) could well compete with the zwitterion route to give (VI).

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